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CHARACTERIZATION OF COAL SURFACES BY ION MICROSCOPY
PHASE 2: SURFACE OXIDATION

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SSW-022

Characterization of Coal Surfaces

by

Ion Microscopy

Phase 2: Surface Oxidation

Final Report

by

R. R. Martin and N.S. McIntyre

Surface Science Western

University of Western Ontario
London, Ontario N6A 5B7

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Forward

As those involved in directing this series of studies have learned more about the characterization of coal, it has become clear that experiments which depend upon a new technique such as ion microscopy, must be constantly referenced to techniques already proven in the field, such as petrographic analysis. It is a a plesure to acknowledge the efforts of Dr. C.G. Winder and Miss K. Aye for their well-coordinated petrographic identification of specific microscopic structures. Mr. W.J. Chauvin and Ms. D. Johnston operated the ion microscope (Secondary Ion Mass Spectrometer) and provided the numerous spectra and ion images essential for this study. Ms. Laurie Harnick built the glass reaction vessel used for oxidation studies. Finally, we thank our Scientific Authority, Dr. A.J. MacPhee for his advice and encouragement.

Summary

A method for the low temperature oxidation of microscopic structures within coal surfaces has been developed using isotopic oxygen ($^{18}O_2$) as a tracer, and Secondary Ion Mass Spectrometry (SIMS) as a surface analysis technique. The uptake of oxygen in coal has been studied as a function of maceral type, coal rank, oxidation time and temperature.

The uptake of ^{18}O onto most coal surfaces can be detected after exposure to $^{18}O_2$ for less than 1 hour at 100°C. The measured fixation of tracer oxygen is significantly higher in fusinite than in vitrinite. The rate of uptake of ^{18}O is a strong function of the rank and maceral type. Significant proportions of tracer oxygen are removed from the surface by pumping, but even some of the off-gas was shown to have reacted with the coal surface. Chemical oxidation of coal was also studied, and the results differed significantly from those of the gas phase process. The microscopic structures within several areas of one coal (P-250) were analyzed by SIMS to determine possible mineral structures. This was accomplished using reference minerals which gave characteristic relative ion intensities for each structure. In several areas, clay minerals could be identified as sources of the major inorganic constituents and it is suggested that the widespread presence of such clays in fusinite could catalyze the uptake of oxygen.

CHAPTER 1

STATEMENT OF WORK

Ion Microscopy, a type of Secondary Ion Mass Spectrometry, is a highly sensitive analytical technique capable of detecting virtually all chemical elements in microscopically small regions. It is considered a promising approach to characterizing the complex heterogeneous structures typical of coal.

The Cameca IMS-3F Ion Microscope in the Surface Science Laboratory (unique in Canada) is to be used to evaluate the potential of coal micro-analysis. This particular model of Ion Microscope is considered the most technically advanced available with a capability of detecting many elements in the part per million range. Analytically difficult elements such as carbon and hydrogen are also detectable and their distribution determined to a resolution of 0.5 um. Thus, both organic and inorganic phases can be characterized.

TASKS

1. Examine four (4) fresh Coal from Eastern and Western Canada (characterization of macerals, vitrinite, fusinite, semi-fusinite).
2. Examine the same four (4) fresh-coals after being subjected to laboratory oxidation in order to characterize the changes taking place during oxidation.
3. Examine four (4) additional naturally oxidized coals from Western Canada.

4. All 12 of the above samples will be examined using Ion Microscope techniques with ion images of various portions of the samples as given in the report for Phase I of this work. In addition to this all regions examined by ion microprobe will be examined using reflected light optical microscopy and photo-micrographs made of each region. This is vital to this study to enable petrographic (i.e. maceral) identification of all regions under investigation. Optical and ion images of all samples examined will be provided by the investigator.

CHAPTER 2

BACKGROUND

Coal is a remarkably complex and heterogeneous substance consisting of a wide variety of organic, inorganic and organometallic phases. These occur in intimate mixtures and are difficult to characterize. The increased use of coal as a fossil fuel has led to an intensification of research into its structure and reactivity. Particular attention has focussed on the low temperature oxidation of coal [1-3], both because of problems associated with the coal combustion, and the changes in physical properties [4] associated with the low temperature oxidation (weathering). Low temperature oxidation is also of interest because of the risk of spontaneous combustion in coal stockpiles [5]. There is some evidence that indwelling mineral matter plays some catalytic role in the oxidation process [6], and as a result there is considerable interest in the origin, distribution and chemical nature of minerals and of inorganic species in general in coal.

A variety of experimental techniques have been brought to bear on coal characterization. This report describes the use of Secondary Ion Mass Spectrometry (SIMS) to study the low temperature oxidation and mineralization of coal. SIMS involves the mass spectrometric analysis of ions removed from a surface by the action of a focussed primary ion beam. The secondary ions produced are characteristic of all the elements present and may be identified by their mass numbers and isotope ratios. Unique surface information is provided by the very high detection sensitivity. The ppb to ppm range is often achieved. This extends to low atomic number elements which are difficult or impossible to detect by other surface spectroscopies.

SIMS (also sometimes called Ion Microscopy) has a strong capacity for analysis of microscopic regions. The small diameter to which the primary ion beam can be focussed allows SIMS spectra to be obtained for regions only 20-50 um in diameter.

In addition, ion optics can be used to create an image of the secondary ion spatial distribution, often yielding a dark space resolution better than 0.5 um. Vertical information is obtained by allowing the primary ion beam to penetrate, by sputtering, the sample surface, and measuring the secondary ion intensities as a function of time. These techniques have been used with other geological materials [7], polymers [8], organometallics [9] and biologican materials [10] as well as coal. The use of SIMS in the investigation of coal has been largely pioneered in this Laboratory. Our work to this point is reported elsewhere [11-14], and may be summarized as follows:

SIMS has been used to analyze the organic and inorganic constituents of selected coal surfaces. Negative ion mass spectra are found to produce information more characteristic of the organic components of the coal, while the inorganic elements present are better determined using positive secondary ion spectra. The spatial distributions of a number of inorganic elements and carbon, hydrogen and oxygen have been imaged. Negative ion images of carbon polymers appear to be particularly useful for providing structural detail of the coal surface and certain chemical differences can be recognized from the distribution of different molecular ions of carbon.

Fusinite macerals have been found to be particularly enriched in oxygen and fluorine [13]. Photoelectron spectroscopy has been used in conjunction with SIMS in this maceral-type to confirm the presence of carbon monofluoride. The speciation of elements between coal macerals and between organic and

inorganic phases has been found to be particularily marked in fusinite where the cell structures provide convenient sites for epigenetic mineral formation.

A major challenge in this analysis of SIMS spectra has been the presence of a large number of molecular ions. This difficulty has recently been eliminated by the development of a method for achieving nearly complete secondary ion suppression [7]. This development has been important in allowing the use of ^{18}O as tracer in the study of low temperature oxidation without interference from H_2O^+ secondary ions.

These previous studies have made possible the research reported here, in which the low temperature oxidation of coal was studied using ^{18}O to probe the reactivity of a specific coal as a function of maceral type and carbon content. Oxidation with chemical oxidants was also studied as was the ability to detect changes in the organic material in the coal as a result of chemical oxidation. This report also describes the use of SIMS in an examination of the geochemistry of the coal made with a view to establishing some relationship between the inorganic material and subsequent oxidation of the coal.

This report is thus divided into three parts which cover three related SIMS studies of coal: Oxidation using an oxygen tracer, the chemically-induced oxidation of coal and SIMS studies of coal geochemistry.

CHAPTER 3

SIMS STUDIES OF COAL OXIDATION USING AN OXYGEN TRACER

A. INTRODUCTION TO THE STUDY

In this chapter the low temperature gaseous oxidation of a number of well-characterized coal specimens has been studied using tracer oxygen techniques combined with a SIMS method which is sensitive to the presence of the tracer on the coal surface. The effects of maceral type, rank, oxidation temperature and oxidation time are explored, as is the effect of vacuum treatment of specimens.

B. EXPERIMENTAL

Coal specimens used in this study, supplied by the Scientific Authority at CANMET, were chosen to provide a wide range of carbon contents (rank), and maceral types. The selection thus permitted comparative studies of oxidation and/or mineral content to be made as a function of both rank and maceral type. No identification of the origin of these coals was originally supplied by the Scientific Authority.

Immediately before use, the coal was cut with a diamond saw, perpendicular to the bedding, then polished on a silk wheel using diamond grit as the abrasive material and water as lubricant. This prevented the introduction of hydrocarbon impurities from lubricating oils and contamination of the surface with abrasives such as alumina.

The higher rank coals required no further preparation but mild dewatering was required before the lignites could be used because of the high vacuum requirements of the SIMS instrument. This treatment was kept to a minimum to avoid perturbing oxidation mechanisms which might involve water,

typically maintaining the sample under vacuum overnight was sufficient. Petrographic analysis was carried out using a Zeiss optical microscope with Zonax computer control.

Coal samples with freshly cut and polished surfaces were oxidized in a 25 mm bore glass tube furnace. Before oxidation the tube was evacuated to $5X10^{-3}$ torr and 91% $^{18}O_2$ (Merck, Sharpe & Doehm Ltd.) was introduced until the desired pressure was measured using a mercury manometer. A massive copper cylinder was placed around the sample tube and the entire assembly was heated to the desired temperature using a resistive winding. Gas products of the reaction were able to be cold-trapped in a sidearm flask and later analyzed with a Varian MAT 311-A mass spectrometer.

SIMS analysis of the ^{18}O uptake was carried out using a Cameca IMS-3F ion microscope normally using an O^- primary ion beam from a duoplasmation ion source. The mass filtered primary ion beam with an accelerating voltage of 12.5 keV and an ion current between 50 and 100 nA was focussed into a 50-100 μm spot. Specimen isolation (SI) [7] conditions were achieved by isolating the speicmen electrically using a 1 mm teflon spacer between the specimen and the top plane of the specimen holder. A tantalum mask with a 5 mm diameter hole was secured above the specimen and attached electrically to the stage. During the experiment, the specimen potential was allowed to float freely.

Some SIMS studies also made use of a Cs^+ primary beam with a specimen which was grounded and surface coated with gold to prevent charging.

C. RESULTS

[a] Effects of Oxidation Temperature

The first set of results were intended to examine the scope of usefulness of ^{18}O as a tracer for oxidation of coal and to investigate the effect of oxidation temperature. Five pieces of coals from a group labelled P-250 were heated in $^{18}O_2$ at 0.4 atmospheres to temperatures of 100°, 155° and 200°C. Those obtained for the coal heated to 100° and 155°C were from regions which had been fully characterized petrographically.

Figures 1(a) and (b) show positive secondary ion mass spectra, taken under SI conditions of a vitrinite surface in coal P-250. The spectra were taken at adjacent locations on the maceral surface before and after the coal was oxidized in ^{18}O at 100°C for 72 hrs. Before oxidation, no peak at m/e = 18 can be detected (Figure 1(a)), thus showing that contributions from the interferring $H_2{}^{16}O^+$ molecular ion had been successfull suppressed. After oxidation (Figure 1(b)) a peak is detected at m/e = 18 which is ascribed to the presence of ^{18}O within the coal surface. The SIMS spectrum showing ^{18}O uptake in an adjacent fusinite maceral is shown in Figure 1(c).

All mass spectra were taken during the first 60 seconds of exposure of the surface to the primary ion beam, and during this period the beam would be expected to have penetrated the surface to a depth of 10-20 nm (100-200 Å). Thus all measurements reported can be considered as a sampling of the coal surface at a depth of 10±5 nm. The intensity of $^{18}O^+$ measured was normalized to the intensity of other secondary ions by ratioing the $^{18}O^+$ signal to that of $^{12}C^+$.

Table 1

Uptake of ^{18}O in Coals: Effects of Maceral-type and Temperature

Sample Treatment	^{18}O Uptake ($^{18}O/^{12}C$)				
	Vitrinite	Fusinite	Semi-Fusinite	Exinite	Micrinite
1. 60 h at 100°C	8×10^{-4}	3×10^{-3}	-	-	6×10^{-3}
2. 60 h at 100°C	9×10^{-5}	3×10^{-4}	-	-	-
3. 60 h at 100°C[1]	3×10^{-4}	5×10^{-3}	3×10^{-3}	-	-
4. 72 h at 155°C	2×10^{-3}	9×10^{-2}	-	3×10^{-2}	-
5. 72 h at 200°C[2]	2×10^{-2}	-	-	-	-

1. Coal stored under water until ^{18}O oxidation.

2. Maceral was identified as vitrinite.

In Table 1 the uptake of ^{18}O is shown for a number of P-250 coal surfaces containing several different maceral types. The uptake of ^{18}O is clearly detected even at oxidation temperatures as low as 100°C. The average $^{18}O/^{12}C$ ratio for vitrinite is 5×10^{-4} - well above the estimated detection limit of 1×10^{-5}. Of particular importance is the observation that, within each specimen, the uptake of ^{18}O in fusinite is 5 - 10 times greater than in a vitrinite maceral. The precision of the measurements within a single specimen is much better than the between separate specimens largely because of uncertainities in the control of oxidation experiment itself. Even so, there is clearly an increased uptake of ^{18}O detectable within each maceral as the oxidation temperature is raised.

One of the specimens oxidized at 100°C had been kept free of air oxidation prior to its reaction with $^{18}O_2$. This was done by keeping the sample entirely under water from the time it left the mine face to the time it was oxidized in $^{18}O_2$. The ^{18}O uptake for macerals in this specimen (see Table 1) was closely similar to other specimens analyzed, which had all been exposed to ambient oxidation. The differential ^{18}O uptake on fusinite was also similar to that observed for the other specimens.

[b] Lability of Reacted ^{18}O in Coal

One P-250 coal specimen reported in Table 1 (#3) was pumped in a vacuum of 1×10^{-4} torr. for a period of 24 hours. Subsequent SIMS studies showed that 90% of the ^{18}O had been removed from the fusinite maceral after pumping. As a consequence further experiments were conducted to determine the amount of ^{18}O which could be readily removed from the coal through pumping.

A specimen of another coal submitted by the Scientific Authority (P-302) was oxidized in $^{18}O_2$ for 24 hours at 100°C. Following surface analysis with SIMS for ^{18}O content, the specimen was pumped for 6 hrs at a pressure of 5×10^{-4} Torr and reanalyzed. The $^{18}O/^{12}C$ and $^{16}O/^{12}C$ results are shown in Table 2, both before and after pumping. Adjacent areas on each maceral were measured after each procedure. The gases produced during the vacuum pumping stage were collected for analysis.

Table 2

Uptake of ^{18}O in Coals: Effect of Pumping on Reacted ^{18}O

Maceral type	Relative ^{18}O Uptake ($^{18}O/^{12}C$)			
	After Initial Oxidation[1]		After Pumping[2]	
	$^{18}O/_{12C}$	$^{16}O/_{12C}$	$^{18}O/_{12C}$	$^{16}O/_{12C}$
Vitrinite	5×10^{-5}	7×10^{-3}	3×10^{-5}	8×10^{-3}
Fusinite	5×10^{-4}	6×10^{-2}	2×10^{-5}	6×10^{-2}

1. Coal 302 was oxidized in $^{18}O_2$ at 0.2 atm for 23 h.

2. The oxidized coal was actively pumped *in vacuo* at 5×10^{-4} torr. for 6 h.

The relative ^{18}O uptakes in fusinite and vitrinite are seen to be very similar to those obtained earlier in Table 1. Both macerals were found subsequently to lose about 50% of their surface ^{18}O during vacuum pumping. Mass spectrometric analysis of the product gases revealed the following gases as major products (in decreasing order of abundance): $C^{18}O_2$, $C^{16}O_2$, $C^{16}O$, $C^{18}O$, $H_2{}^{18}O$. There is thus good evidence that some

^{18}O released during heating had been bonded chemically to the coal surface during oxidation.

While the ^{18}O uptake in coal clearly varies with the coal composition and reaction conditions, the ratio of $^{16}O/_{12}C$ remains essentially constant (see Table 2). It has been assumed that this was due to the overwhelming present of ^{16}O in the negative primary ion beam used in most of the SIMS studies. To determine if the oxygen detected was associated with the beam or the coal, a $^{133}Cs^{+}$ positive primary beam was used in place of the $^{16}O^{-}$. In a comparison of $^{16}O/_{12}C$ ratios on surfaces before and after the vacuum pumping treatment, no change in ratio was detected. We conclude that much of the ^{16}O intensity really is representative of oxygen in the coal. Assuming that all of the ^{16}O observed in Table 2 originates in the coal the amount of ^{18}O oxidation compared to ^{16}O oxidation is $\sim$1%.

[c] Effect of Coal Rank on ^{18}O Uptake

The uptake of ^{18}O was measured on coals of differing rank (carbon content). The coal specimens were obtained from the Scientific Authority along with their rank values. All uptake measurements were conducted on vitrinite macerals within each coal specimen with two exceptions: no distinct maceral phases could be detected in the lignite specimen, while in specimen P-302 a second measurement was made in a fusinite maceral. All specimens were prepared as previously and were heated at 100°C in 0.2 atm of $^{18}O_2$ for 24 hr.

The measured uptake of ^{18}O in each specimen is given in Table 3.

Table 3

Uptake of ^{18}O in Coals: Effect of Rank

Specimen Number	Description	Maceral type	% Carbon[1]	Relative ^{18}O Uptake ($^{18}O/_{12C}$)
P-732	Lignite	[Lignite]	63	3×10^{-3}
P-668	Sub-Bituminous	Vitrinite	72	2×10^{-3}
P-569	Byron Creek	Vitrinite	88	3×10^{-3}
P-587	Balmer	Vitrinite	90	4×10^{-4}
P-736	Washed Prince	Vitrinite	81	8×10^{-5}
P-302	High Volatile - Bituminous	Vitrinite	87	4×10^{-5}
P-250[2]	High Volatile - Bituminous	Vitrinite	86	7×10^{-5}

1. Carbon was determined on a dry ash-free basis.
2. P-250 fusinite had a relative uptake of 5×10^{-4} under equivalent conditions.

It can be seen that there is a very rough inverse relationship between carbon content and uptake of ^{18}O - the high ranked coals having an uptake two orders of magnitude lower than those of the lowest rank examined. The coals analyzed are divided in Table 3 in groups having ^{18}O uptakes which are statistically significantly different.

[d] Effect of Oxidation Time on Measured Uptake

The ^{18}O uptake as a function of oxidation time is shown in Table 4 for a number of areas of the same coal specimen submitted by the Scientific Authority.

Oxidation was carried out under 0.2 atm of $^{18}O_2$ at a temperature of 100°C. Some better measure of the statistical significance of the measured uptakes is gained from data taken from two sequential mass spectra on each surface. Although the second spectrum represents a depth some tens of nanometres greater than the first measurement, the agreement is fairly good between the ratios derived. A comparison of specimens oxidized for 4 and 4.5 h periods is useful since, in most cases, the only differences between the two should be ascribable to variations in the original specimen or in the oxidation procedure.

Table 4

Uptake of ^{18}O in Coals: Effect of Oxidatin Time

Specimen Number	Maceral type	% Carbon	Relative ^{18}O Uptake ($^{18}O/_{12}C$)			
			1 hr	4 hrs	4.5 hrs	24 hrs
P-732	(Lignite)	48.	$3X10^{-4}$	$3X10^{-4}$	$1X10^{-3}$	$3X10^{-3}$
			$8X10^{-4}$	$2X10^{-4}$	$1X10^{-3}$	$6X10^{-3}$
P-668	Vitrinite	68.	$<1X10^{-5}$	$8X10^{-4}$	$2X10^{-4}$	$2X10^{-3}$
			$<1X10^{-5}$	$1X10^{-3}$	$3X10^{-4}$	$5X10^{-3}$
P-587	Vitrinite	81.	-	$4X10^{-4}$	$1X10^{-4}$	$4X10^{-4}$
P-302	Fusinite	84.	-	$4X10^{-5}$	$7X10^{-5}$	$5X10^{-4}$
				$<1X10^{-5}$		

The increase in surface ^{18}O with time appears to be the most controlled in the low rank lignite (P-732). Even after a 1 hour oxidation the presence of ^{18}O on the surface could be readily detected, and the ^{18}O increased fairly steadily as a function of time during the 24 hour survey period.

The rate of oxygen uptake on higher rank coals is more erratic. For P-587 (81% carbon), surface ^{18}O is first detected after 4 hours of oxidation, but does not change significantly after that time.

[e] Effects of Mineral Inclusions

Using SI-SIMS it is easy to monitor changes in relative concentration of many trace and minor inorganic elements in the coal, at the same time as ^{18}O uptake is being determined. Consequently, in several different fusinite macerals, an attempt was made to correlate ^{18}O uptake with a change in the relative intensities of the two most abundant inorganic ions, iron and sulphur. These two elements are expected to arise partly from pyrite inclusions in the coal. Pyrite itself is expected to be partly oxidized under our conditions and therefore might accelerate oxidation of nearby carbonaceous species. Although the intensities of both these ions varied by more than two orders of magnitude between specimens analyzed, no statistically significant change in ^{18}O uptake could be attributed to changes in concentration of these elements and thus probably to the concentation of pyrite in the coal. Better defined experiments are however planned, where ^{18}O distribution on the surface will be imaged and then correlated with distributions of major inorganic ions.

D. DISCUSSION

Studies of the low temperature ($\sim$100°C) oxidation of coal require sensitive methods capable of detecting small changes in the oxygen content. Most coal already contains sufficient oxygen to mask the addition of further quantities added through low temperature oxidation.

Previously, the change in specimen dilation has been used to measure oxygen changes as small as a few tenths of a percent [15]. The use of the isotope tracer technique with ^{18}O has also been applied to coal oxidation studies previously [16], but it was only able to yield results on the gases produced, not on the oxidized coal itself. The combination of SIMS studies of the coal surface and the use of an ^{18}O tracer, first reported in this work, gives unique sensitivity to the measure of small changes in oxygen uptake. The specificity is not only to the general surface region of the coal, but also to microscopic areas within the surface region. Thus, it is possible to differentiate directly the uptake of oxygen into two or more different maceral types within a single coal specimen.

These present studies have shown that the identification of trace oxygen can be made even at a level of 1% of the existing ^{16}O content of the coal (i.e. 0.1% in a 10% oxide specimen). Moreover, the measurement is made within a few nanometres of the surface where changes in oxygen content are first registered. Consequently in some cases (e.g. lignite) the uptake of the oxygen tracer is detectable after less than one hour of oxidation at 100°C.

The microscopic analytical capability of SIMS has led to a relative measure of oxygen uptake in vitrinite and fusinite macerals, which indicates that, at the very least, the additional oxygen is adsorbed in greater density onto a fusinite surface than that of vitrinite. There is evidence that much of this tracer oxygen is labile enough to be pumped out of the coal in a vacuum, but the product is shown to contain significant isotopically-labelled hydrocarbons which suggest that the labile ^{18}O had been chemically

bonded to the coal, probably in the form of an "oxy coal" compound [17].

There is considerable evidence that, at coking temperatures (600°C), fusinite is less reactive to oxygen than vitrinite. This however, may not be the case at 100°C, particularly if even rather weak chemical bonding is taken into account. There has been no other *in situ* comparison of relative maceral oxidation at 100°C. The only other study which has compared the oxidation of fusinite and vitrinite at 100°C was done under quite different chemical conditions [18]. In this latter work the oxidation was carried out using a permanganate solution on physically separated macerals and under these conditions fusinite was found to be unreactive. Our further work reported below suggests that chemical and gas oxidation produce quite different oxidation results.

Other oxidation effects are easier to reconcile with past experience. There is a rough inverse relationship between rank and oxygen uptake. This has been attributed by other workers to a change in porosity of the coal [19-20].

Increased temperature and oxidation time generally lead to an increased ^{18}O concentration on the surface of the specimen. It is not clear at this point, whether the reaction reflects events only close to the outer surface or whether the tracer oxygen has penetrated well into the bulk of the specimen. Changes in SIMS intensity with depth such as those in Table 4, suggest that oxygen tracer permiation is significant for some specimens. However, depth profile information obtained with SI-SIMS is often not reliable and thus these results must be considered on a surface basis only. Even considering the measurement for surfaces, a considerable scatter in results

is observed which is, we believe, largely due to the heterogeneous nature of the substrate, even within the boundaries of a fairly well characterized maceral. With the 100 um area of analysis used in SI-SIMS, it is difficult to orient the beam in relation to all significant structural and chemical features on the surface.

If ^{18}O intensities could be unambiguously measured under non-SI conditions, e.g. using O_2^+ or Cs^+ primary beams, it would be possible to correlate surface features, such as mineral inclusions with tracer oxygen uptake. Further, polished sections across the oxidized coal face could be studied to measure tracer permiation, as well as the variation in permeation with structure. These and other projects may be accomplished with careful use of the high mass resolution capability of the ion microscope.

E. CONCLUSIONS

The present technique affords a rather crude, semi-quantitative measure of oxygen uptake on a coal surface. It is however the first successful *in situ* measurement of tracer oxygen in coal. Most of the uptake measurement observations are in accord with expected oxidation behavior. However, the uptake of ^{18}O on fusinite surfaces is found to be considerably greater than on vitrinite - an unexpected result. Better quantitation and spacial definition may result in future from the use of high mass resolution, rather than the SI effect, to define the ^{18}O tracer on the surface.

CHAPTER 4

SIMS ANALYSIS OF CHEMICALLY OXIDIZED COAL

A. INTRODUCTION TO THE STUDY

A previous low temperature oxidation study [18] of vitrinite and fusinite macerals used permanganate ion in aqueous solution as the oxidant (see above). It was decided to carry out similar solution oxidation on in situ macerals, using SIMS to determine the local increase in oxygen concentration.

B. EXPERIMENTAL

Two samples of coal P-250 were cut and polished as before and were suspended in concentrated solutions of chromic acid and potassium permanganate for a period of two hours. Half of each piece was not oxidized, thus providing treated and untreated areas for comparison.

SIMS analysis of this coal made use of a 50 um diameter Cs^+ primary beam to insure that no oxygen in the primary beam could interfere. The SI method was not used and the sample was coated with approximately 200A of gold to prevent charging.

C. RESULTS AND DISCUSSION

The intensity ratio of $^{16}O/_{12}C$ was measured within each maceral, both for chemically-oxidized and non-oxidized specimens, and the results are summarized in Table 5.

Table 5

Uptake of ^{16}O in Coals due to Chemical Oxidation: SIMS Analysis of Reacted and Non-Reacted Macerals

Maceral	Treatment	$^{16}O/^{12}C$ Ion Intensity Ratio	
		Oxidized	Chemically Oxidized
Fusinite	$H_2Cr_2O_7$	7	47
Vitrinite		4	4
Fusinite	$KMnO_4$	7	7
Vitrinite		6	25

The permanganate oxidation results support the previous [18] permanganate results carried out on physically separated macerals. With chromic acid however, the results are the opposite.

This casts some doubt upon the relevance of chemical oxidation studies to gas phase investigations.

CHAPTER 5

STUDIES OF COAL GEOCHEMISTRY USING SIMS

A. INTRODUCTION TO THE STUDY

Future studies of coal oxidation will require increased interpretation of the elemental composition and mineral structure in the area of tracer oxygen reaction. It is likely that some minerals will influence the oxidation rate and, consequently it is important to learn more about the use of SIMS to recognize specific mineral distribution in coal. The basis of mineral characterization by SIMS is to identify the constituent elements in the same intensity ratio as in a reference mineral SIMS spectrum. In this chapter the SIMS spectra of a series of clay minerals have been studied and an attempt has been made to apply the results to the identification of certain minerals in coal P-250.

Clay minerals are difficult materials to characterize. They are non-stoichiometric, have variable water content and contain exchangeable ions, whose concentrations are a function of groundwater concentration with which they have been in contact. Clays undergo weathering after long contact with groundwater, and silicon and alkali elements are gradually lost to solution. A typical weathering sequence for smectite , a clay mineral found frequently in coal, would be:

Smectite → Illite and/or Kaolinite → Gibbsite

It is reasoned that if SIMS could identify the ion intensity ratios typical of each clay, the degree of weathering of the coal could be determined, and from this could come better information on the processes responsible for coal formation.

B. EXPERIMENTAL

Powdered clay reference materials were obtained from the Department of Geology and were pelletized. The same coals described in Chapters 2 and 3 were used as examples of clay-bearing coals. For SIMS imaging studies using an O_2^+ primary beam, the polished coal specimens were coated with a thin gold film.

SIMS conditions used for SI measurements were the same as for previous investigations, while for non-SI conditions a 50 um O_2^+ 6.5 keV (net) beam was rastered over a 250 X 250 um surface. Ion images were obtained usually within a 150 um imaged field and the images, displayed on the spectrometer phosphorescent screen, were photographed on 35 mm Ektachrome film. In addition to petrographic analysis, some specimens were microscopically analyzed using an ISI DS-130 Scanning Electron Microscope.

C. RESULTS AND DISCUSSION

[a] SIMS Studies of Reference Clay Minerals

SIMS spectra (SI and non-SI) were taken of the minerals smectite, illite, kaolinite and gibbsite. Using aluminum as a reference the ion intensity ratios for silicon, sodium and potassium are given in Table 6 for the four minerals.

Table 6

SIMS Ion Intensity Ratios from Spectra of Reference Clay Minerals

Clay	Nominal Formula	Ion Intensity Ratios		
(a) SI Mode		$\frac{^{28}Si^+}{^{27}Al^+}$	$\frac{^{23}Na^+}{^{27}Al^+}$	$\frac{^{39}K^+}{^{29}Al^+}$
Smectite	$Al_2Si_4O_{10}(OH)_2H_2O$	1.5	$2.0X10^{-2}$	$<4.0X10^{-3}$
Illite	$KAl_2(AlSi_3O_{10})(OH)_2$	1.1	$1.0X10^{-2}$	$6.7X10^{-3}$
Kaolinite	$Al_4Si_4O_{10}(OH)_8$	0.5	$1.0X10^{-4}$	$0.3X10^{-3}$
Gibbsite	$Al(OH)_3$	$9X10^{-4}$	$8X10^{-4}$	$8X10^{-6}$
(b) "Normal" or Non-SI Mode				
Smectite	$Al_2Si_4O_{10}(OH)_2H_2O$	0.9	$80X10^{-2}$	$10X10^{-2}$
Illite	$KAl_2(AlSi_3O_{10})(OH)_2$	0.6	$15X10^{-2}$	$17X10^{-2}$
Kaolinite	$Al_4Si_4O_{10}(OH)_8$	0.7	$1.3X10^{-2}$	$5X10^{-2}$
Gibbsite	$Al(OH)_3$	0.02	$3X10^{-2}$	$1.2X10^{-2}$

The ratios obtained under SI conditions exhibit much more definitive differences between the mineral than do the ratios taken under normal (low kinetic energy) conditions. Illite and smectite having roughly comparable Al^+/Si^+ ratios, are best distinguished by the presence of potassium ion. Kaolinite contains the same elements as smectite and as such, the two minerals should be difficult to distinguish. However the more rapid exchange of sodium with smectite results in a considerably higher sodium

concentration in this mineral than in kaolinite. Gibbsite is, of course, distinguished by the absence of major ions other than aluminum. Thus, with care, the four minerals in a particular weathering sequence can be distinguished.

[b] SIMS Analysis of Specific Coal Mineral Phases

Elemental microstructure in coal can be analyzed by SIMS in two ways. Firstly, mass spectra of specific small areas (typically ~50 um diameter) can be obtained. Secondly, secondary ion microscopy of the region can be carried out. The latter approach is a particularly promising technique for studying the elemental distribution in coal samples [11], and hence elucidating coal geochemistry. Accordingly, four distinct areas were selected within typical coals and an analysis of these areas was carried out using ion microscopy and mass spectrometry. Area 1, within a piece of P-250 vitrinite was found to be rich in mineral matter during a random imaging survey. Area 2 was used because a well-defined mineral inclusion had been identified using scanning electron microscopy and an attempt was made to use SIMS to identify the mineral matter. Area 3 was within a large, well-defined fusinite maceral and was selected to examine the expected mineralization within the cellular structure of the fusinite. Area 4, within a well defined P-250 vitrinite maceral, was selected as being likely to be typical of homogeneous vitrinite of the P-250 series.

(i) Area 1

The ion images from this mineral-rich area are shown in Figures 2, 3 and 4. Figure 2 is used to examine the organic region of the coal, delineated by the yield of C^+ (12^+). Figure 3 outlines an alumino-silicate phase

defined by the $Al^+(27^+)$ image. Figure 4 shows the distribution of inorganic elements not related to the alumino-silicate region.

The organic region is not homogeneous (see Figure 2). A portion of the carbon-rich region yields a higher intensity of C_2^- secondary ions, and this same region also gives stronger yields of H^-, O^-, OH^- and F^-. The O^- distribution, while more generalized than the rest, is still strongest in the C_2^- region. Our previous report (11) also pointed out a strong correlation between C_2^- yield and the oxygen ion (O^-) intensity.

The alumino silicate region (Figure 5) is characterized by similar intensities of Al^+ and Si^+, as well as strong intensities of H^+ and O^+. Li^+, Mg^+ and Fe^+ ions are detected from this phase, as is Na^+ (not shown) and all these elements suggest a clay structure. The relative intensities, Na^+/Al^+ and Li^+/Al^+ are sufficiently high (> 0.1) that the clay structure is believed to have undergone little weathering.

Figure 6 gives the distributions of a series of elements which are not associated with the alumino-silicate region outlined by Figure 5. The notable exception is 56^+ which appears to be a mixture of Fe^+, associated with the alumino-silicate phase, and CaO^+ (mass 56) which coincides with Ca^+. The Ca^+ image agrees well with those of Sr^+ and Ba^+, while the distributions of Ti^+ and Ga^+ cannot be readily identified with those of any of the previous elements. These images may represent a set of discrete mineral phases or may represent local enrichment within the widely distributed alumino-silicate region.

High yields of both O^+ and H^+ ions appear indicative of a clay-like structure. The intensity of O^+ from clay reference compounds is 1-2 orders of intensity higher than within the organic phase of the coal. Moreover, we find a relatively high yield of H^+ in clays ($H^+/Al^+ = \sim 0.1$), which is found to be about two orders of magnitude higher than the H^+/Al^+ ion ratio from an alumino-silicate rock mineral such as plagioclase. This is attributed to water in the clay, as well as the many H^+ exchange sites in the clay structure. These approaches thus further improve the means for identifying claylike minerals in the coal.

(ii) Area 2

A Scanning Electron Micrograph (SEM) image of the second area to be examined is shown in Figure 5, together with the energy dispersive X-ray fluorescence (EDX) spectrum from the area. It is clear that the central feature represents a minor inclusion in the coal containing Al and Si as the primary inorganic elements.

Figure 6 shows the SIMS mass spectrum of the central 8000 um^2 of the same area. A much larger number of elements are detected than by EDX. These additional elements are present in concentrations below the EDX detection limits; in addition however, the SIMS ability to detect elements such as hydrogen, carbon and oxygen is useful in identifying the mineral content of this region.

Ion images of the same area are particularly informative. Figure 7(a) shows the distribution of Si^+ ions, which is identical in shape and similar in intensity with that of Al^+ (Figure 7(b)). These ions are confined exclusively to the central region defined in the SEM image. Figure 7(c) shows the distribution of H^+ on the surface.

The H^+/Al^+ intensity ratio can be inferred to be $\sim$0.1, assuming reciprocal response of the photographic film over this range of intensities. Thus, the alumino-silicate structure is likely a clay mineral. Figure 7(d) shows the distribution of sodium and comparison of relative image intensities shows that the Na^+/Al^+ ratio is $\sim$0.1 in the central alumino-silicate zone. From Table 6(b), the most likely clay mineral ($\frac{Na^+}{Al^+} = 0.01$) is kaolinite. The intensity of sodium in the surrounding minerals is considerably higher. Calcium (Figure 7(e)) is found exclusively in the periphery of the analyzed area.

The central feature is likely kaolinite, an alumino-silicate clay mineral with no potassium or calcium detected and very little sodium. This indicates an advanced stage of weathering. The widespread occurrence of kaolinite in coal is well documented [21, 22]. The surrounding material, with its relative abundance of magnesium and calcium coupled with a weak C image and localized inclusions of Na and K, would be expected from epigenetic carbonate minerals [23]. The presence of sodium and potassium indicates that this material has undergone relatively less weathering than the kaolinite.

(iii) Area 3

This region was selected to lie within the boundaries of a well-defined fusinite maceral. The images show the fusinite, as expected [24], to be rich in mineral matter relative to the vitrinite maceral chosen for Area 4 (see below). Figures 8 and 9 show representative ion images; Figure 8 shows those of the major elemental constituent, while Figure 9 shows elements present in more minor concentrations. The C^- and H^- (Figure 8(a) and (b)) define the areas higher in organic concentration, while the Al^+, H^+ and O^+ (Figures

8 (d) - (f)) outline those complementary regions relatively more concentrated in alumino-silicates; the image for Si^+ (not shown) is identical in distribution to that of Al^+ and is of approximately equal intensities.

At closer inspection of Figures 8 and 9, a number of chemically distinct regions can be identified. These are summarized in Table 7. The most prevalent

Table 7

Summary of Chemically Distinct Phases observed within Area 3 (Fusinite) of Coal P-250

Phase No.	Relative Area*	Elements Present+	Comments
1	100% but low intensity	Ca	A weak Ca^+ signal found throughout the area surveyed.
2	10%	C, H	A carbonaceous phase containing low oxygen and few trace elements.
3	60%	Al, Si, Fe Mg (0.1), Na (0.1) K (0.01) C	The intense H^+ image of this region suggests a clay and the presence of sodium and magnesium suggests a relatively non-weathered clay containing iron. The clay contains some carbon. The H image suggests the phase is porous.
4.	< 5%	Na, K	This phase is found within the porous areas of Phase 3. It may be a leaching product of that phase.
5.	5%	Ca, F	The occurrence of these two elements suggests CaF_2

* Area relative to total 5600 um^2 area surveyed.

+ Detection limit is $\sim 5X10^{-2}$ of strongest intensity.

of these is an iron alumino silicate clay-like phase. Certain of the ion images of this phase show porosities within which are located higher concentrations of sodium, perhaps leachate from the clay. In viewing such ion distributions and inferring phase information from them, it must be remembered that each of these inorganic phases is still mixed intimately with carbon. In the case of this fusinite it is estimated that in order to be imaged as an apparent solid intensity these inorganic clays must be particles of one um or less. In the case of calcium, with its almost universal distribution, the origin is likely from cell walls, as was discussed in our previous report [11]. The presence of CaF_2 in fusinite was also identified previously [11].

Thus, much of the fusinite contains a phase with submicron particles of clay-like mineral material in intimate contact with carbon. It is this area which is thought most likely to be susceptible to oxidation, and this will be explored in the future using imaging of ^{18}O distirbution in oxidized fusinite.

(iv) Area 4

The images in Figure 10 were taken within a well-defined band of vitrinite. The intensity of the inorganic ions is 50-100 times lower than the same ions from Area 3. This is related to the overall density of inorganic mineral particles in the coal matrix. The Al^+ and Si^+ (not shown) images correlate well, as do the images of Ca^+ and O^+ (not shown). The sodium and iron distributions do not, in general, match those of the silicon. There is thus insufficient data to judge the mineral constitution of the

isolated particles in this area. The individual particle size may be as large as 5 um, but is usually considerably less. Such particles are likely of detrital origin.

D. CONCLUSIONS

A survey of the inorganic elements in coal P-250 has led to the tentative identification of alumino silicate clay minerals in several regions. The identification is based on elemental intensity ratios which characterize a weathering sequence of clays. The presence of relatively large concentrations of H^+ distinguish clays from other alumino silicate minerals, such as feldspars. Further, the extent of weathering of the clay can be estimated from the relative concentration of sodium - a readily leachable ion.

Three of the four areas analyzed contained areas which were fairly heavily mineralized. The most concentrated mineralization occurred in Area 2 where the alumino silicate was readily detectable by SEM-EDX micro-analysis. In other cases, the clay is clearly distributed as finely divided particles (sub-micron) within a carbonaceous phase. We believe that this mineral phase within the maceral fusinite could assist its rate of oxidation by the availability of catalyst-like surfaces readily dispersed throughout the porous carbanaceous phase.

CHAPTER 6

GENERAL CONCLUSIONS

With the aid of SIMS, we have been able to monitor, for the first time, the uptake of tracer oxygen into localized areas on a coal surface. A series of experiments have shown that the amount of isotopic oxygen detected is usually reproducible to within a factor of two. Given the variance in any surface of petrographically characterized coal, and the reproducibility of the oxidation experiment itself, the agreement observed is considered very satisfactory. The oxygen uptake at 100°C varies inversely with the carbon contenct (rank) of the coal, and this agrees with past studies of the low temperature oxidation of coal of different ranks. Further, there is in most circumstances a measured increase in the tracer oxygen content and the uptake is increased at higher temperature. There is persistent evidence that, under our conditions, fusinite macerals are oxidized more completely than vitrinite, and the rate of oxidation of fusinite is probably greater. This later observation conflicts with some earlier studies of the chemical oxidation of coal in solution at the same temperature. However, in a series of similar chemical oxidation experiments, we have shown that chemical oxidation is very reagent-specific, and thus such studies likely bear little relevance to the low temperature gas phase oxidation of coals.

We have suggested that the higher oxidation of fusinite is linked to the higher mineral content and porosity of this maceral. In a series of ion microscopic studies the inorganic elemental distributionswithin a number of areas in coal P-250 were surveyed. Using some model compounds, much of the

content in several regions was consistent with the presence of clay minerals in different stages of weathering. Finely-divided clay mineral particles are found comminuted through much of the fusinite and its presence might be expected to catalyze carbon oxidation. By contrast, in vitrinite, inorganic elements are found in separated pockets whose overall density is much lower than in the fusinite.

There is sufficient variation in the clay mineral content within fusinite to test the theory relating oxidation rate to mineral content. However, such experiments require a SIMS capability for imaging the distribution of ^{18}O under relatively high spatial resolution. We believe that this will be possible using a cesium primary ion beam and the improved imaging sensitivity recently installed in our Cameca ion microscope. As part of this, however, a better quantitative measure of image intensities are required. In this present work we have attempted at times to measure by eye relative intensities of different elements in an ion image, and infer, from this, a composition. It is possible to derive a truly quantitative comparison of intensities using digital image processing and steps to test such procedures have already been taken. using some microscopic regions of a fusinite area to test the possibility.

While the above procedures will result in improved lateral resolution, little has been said about the measure of tracer oxygen as a function of depth into the coal. The present results suggest that there is permeation to a depth of several tens of nanometres over the oxidation time studied. The rate of oxidation will be determined by the porosity of the material

and it is expected that, in contrast to crystalline solids, oxidation permeation will be rapid. The SI SIMS measurements made in this present work are not well suited to profiling, because of the slow rate of penetration of the primary beam, and because of the rather poor depth resolution obtained with this approach. Our future cesium ion bombardment studies, measuring mass-resolved $^{18}O^-$ secondary ions should give a better measure of the depth and distribution of the tracer oxygen.

Much of the tracer oxygen absorbed by the coal in oxidation experiments could be rapidly removed by extended pumping. However a portion of the oxygen came off the coal as a reaction product - mostly $C^{18}O_2$ or $C^{18}O$. Thus, the ready removal of tracer from the coal does not mean that chemical bonding and reaction did not occur during oxidation. The absence of mixed ^{16}O-^{18}O species suggests that the ^{18}O does not exchange with ^{16}O sites already in coal. Future quantitative analysis of product gases will help to determine the proportion of volatile and non-volatile products during low temperature oxidation.

Thus, the initial study of coal oxidation has suggested many exciting areas for future study.

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LIST OF FIGURES

(1) SIMS positive ion spectra of vitrinite and fusinite macerals in coal specimen P-250 taken under Specimen Isolation (SI) conditions. Spectra were taken before and after oxidation of the vitrinite maceral in $^{18}O_2$. (a) Vitrinite before oxidation (b) Vitrinite after oxidation (c) Fusinite after oxidation.

(2) SIMS ion images for elements associated with organic structure in Area 1 in coal P-250. The signed numbers refer to the mass and charge of the ions detected. The imaged field in all cases is 150 um.

(3) SIMS ion images for elements associated with alumino-silicate mineral structure in Area 1 of coal P-250.

(4) SIMS ion images for elements not associated with the alumino-silicate mineral structure in Area 1 of coal P-250.

(5) Energy dispersive X-ray fluorescent spectrum of Area 2 in Coal P-250. The heavily mineralized area analyzed is shown inset in a Scanning Electron Microscope image.

(6) SIMS positive ion spectrum of Area 2 from coal specimen P-250. The spectrum was taken under Specimen Isolation Conditions and thus most molecular ions are strongly suppressed.

LIST OF FIGURES (continued)

(7) SIMS positive secondary ion images of Area 2 from coal specimen P-250. Images were taken under normal (non-SI conditions): (a) Si^+(2s), (b) Al^+(2s) (c) H^+(18s) (d) Na^+(27s), (e) Ca^+(15s).

(8) SIMS secondary ion images of Area 3 (fusinite) from coal specimen P-250 - Group 1 (non-SI conditions): (a) C^-(2s), (b) H^-(2s), (c) O^-(xs) (d) Al^+(0.5s) (e) H^+(5s) (f) O^+(30s).

(9) SIMS secondary ion images of Area 3 (fusinite) from coal specimen P-250 - Group 2 (non-SI conditions): (a) Ca^+(10s), Na^+(5s) K^+(60s), F^-(30s), Fe^+(0.5 s), Mg^+(5s).

(10) SIMS secondary ion images of Area 4 (Vitrinite) from coal specimen P-250 (non-SI conditions): (a) Si^+(36s) (b) H^+(9s), 9C) Li^+ $(36s)^+$, (d) Ca^+ (27s) (e) Fe^+(27s) (f) Na^+(15s).

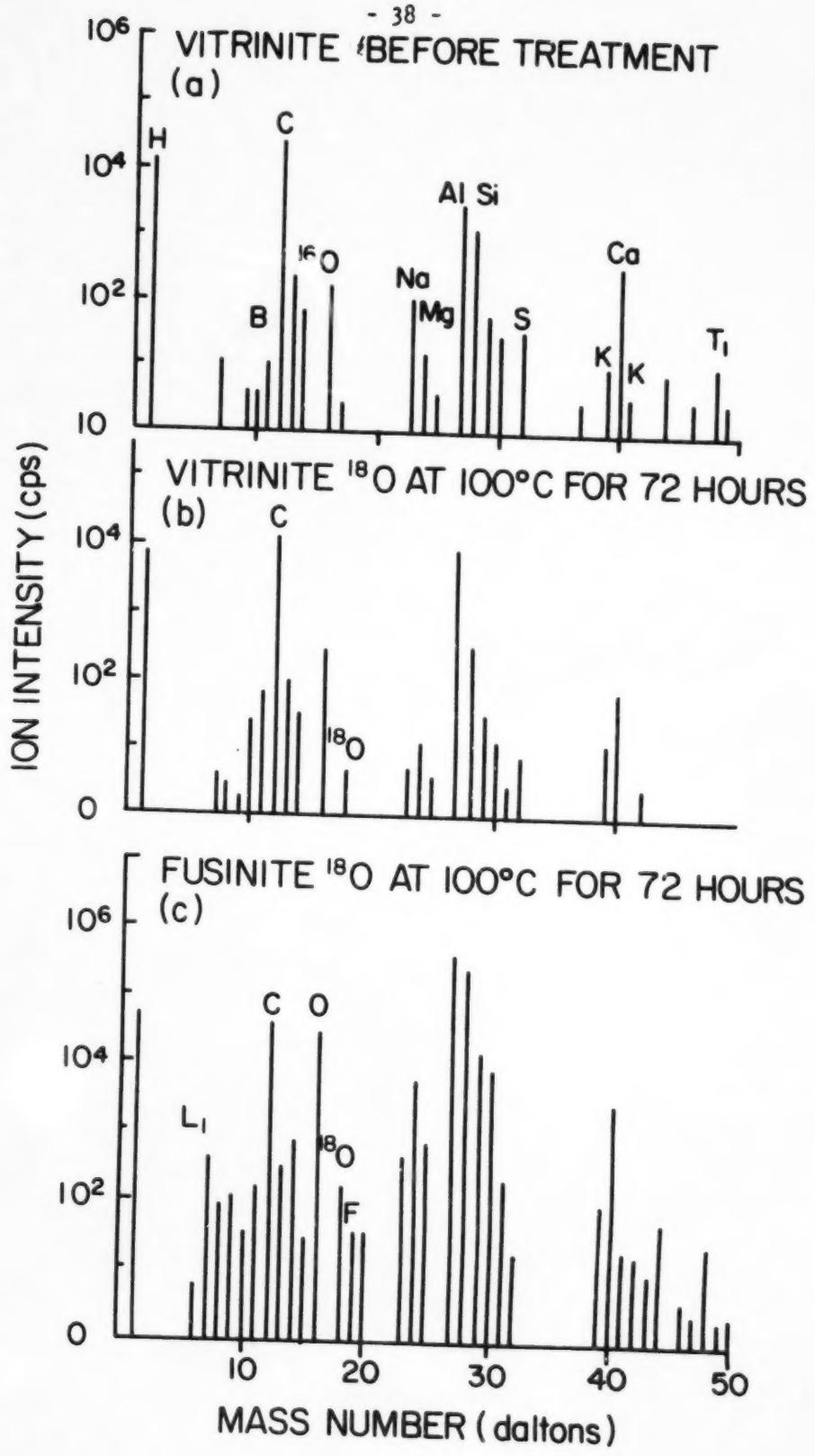
VITRINITE BEFORE TREATMENT
(a)
H
C
B
16O
Na
Mg
Al
Si
S
Ca
K
K
Ti
VITRINITE 18O AT 100°C FOR 72 HOURS
(b)
C
18O
FUSINITE 18O AT 100°C FOR 72 HOURS
(c)
C
O
L1
18O
F
ION INTENSITY (cps)
MASS NUMBER (daltons)

FIGURE 1

FIGURE 2

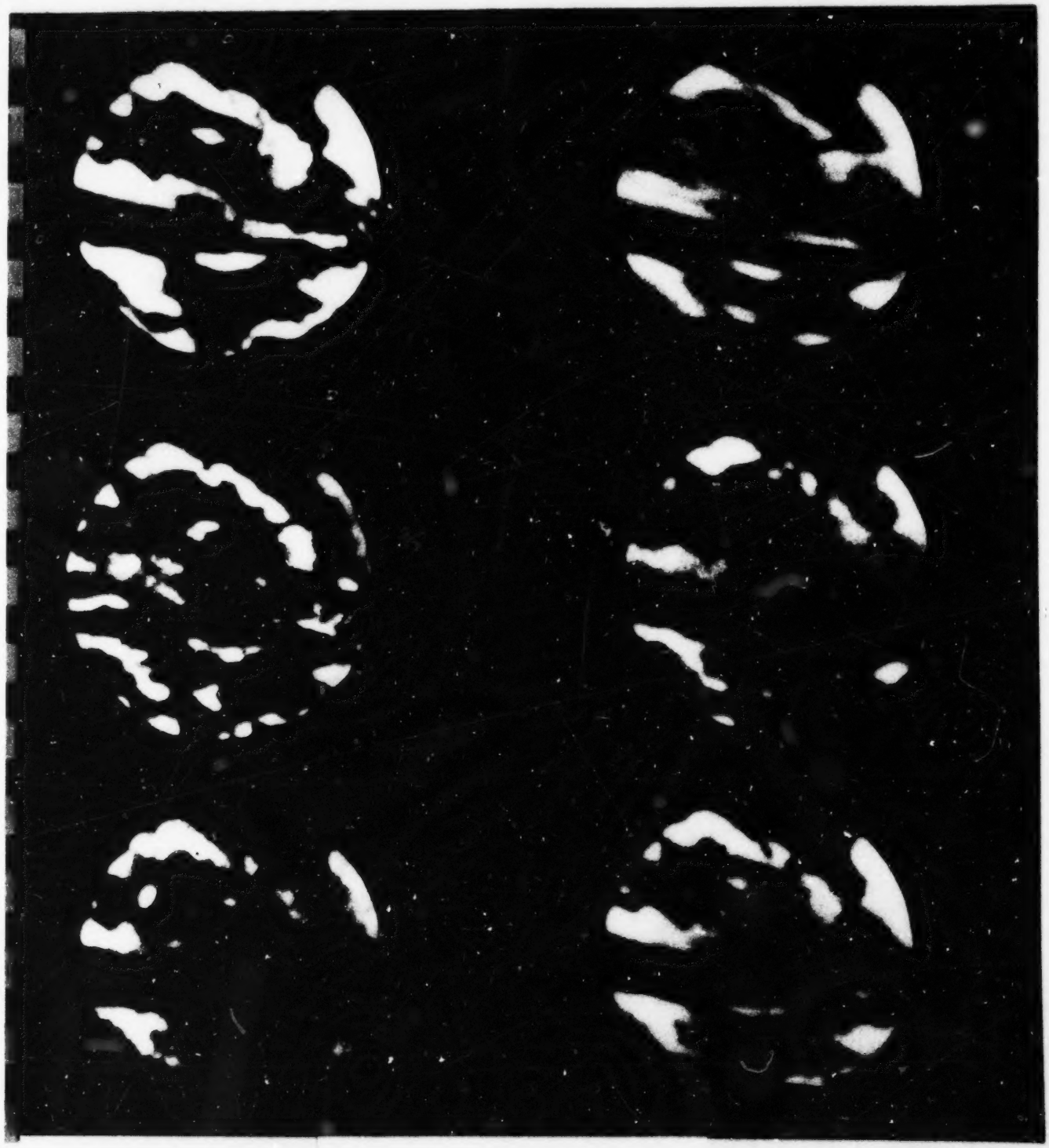

FIGURE 3

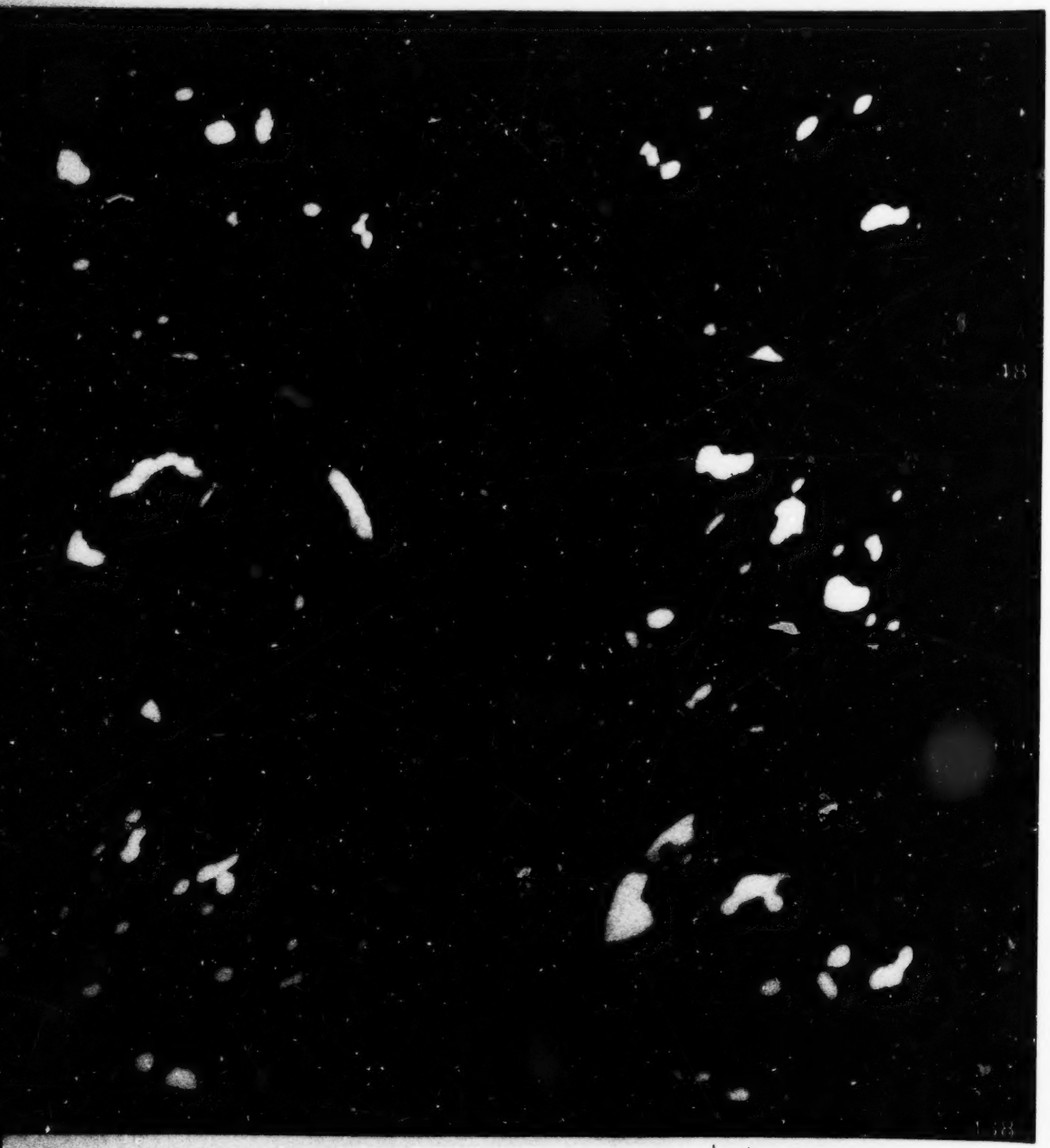

FIGURE 4

X-ray Fluroescence Spectrum of Area 2 in Coal P-250. A Scanning Electron Micrograph of the Heavily Mineralized Area is shown in the Inset

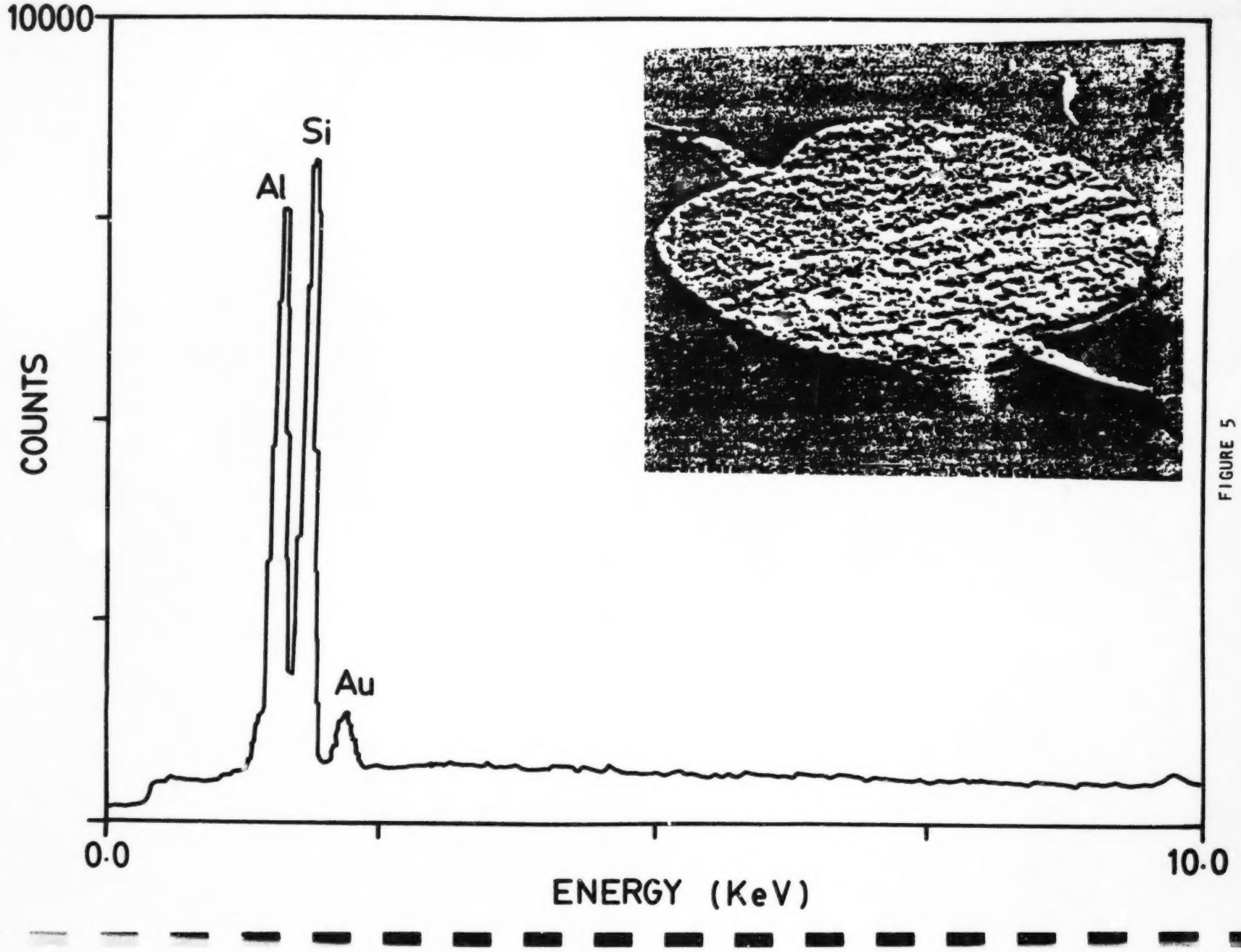

FIGURE 5

SIMS Positive Ion Spectrum of Area 2 from Coal Specimen P-250. The Heavily Mineralized Area is shown in the inset in Figure 5

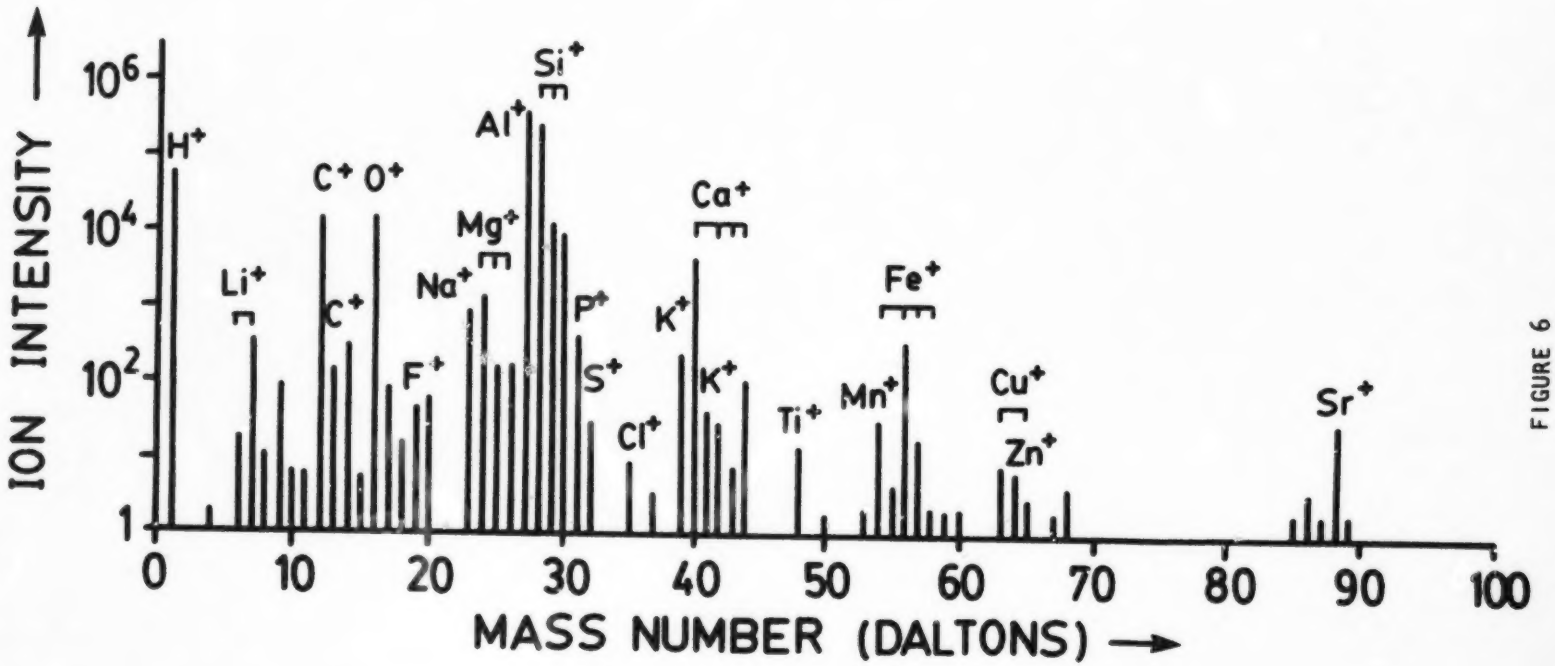

FIGURE 6

Figure 7

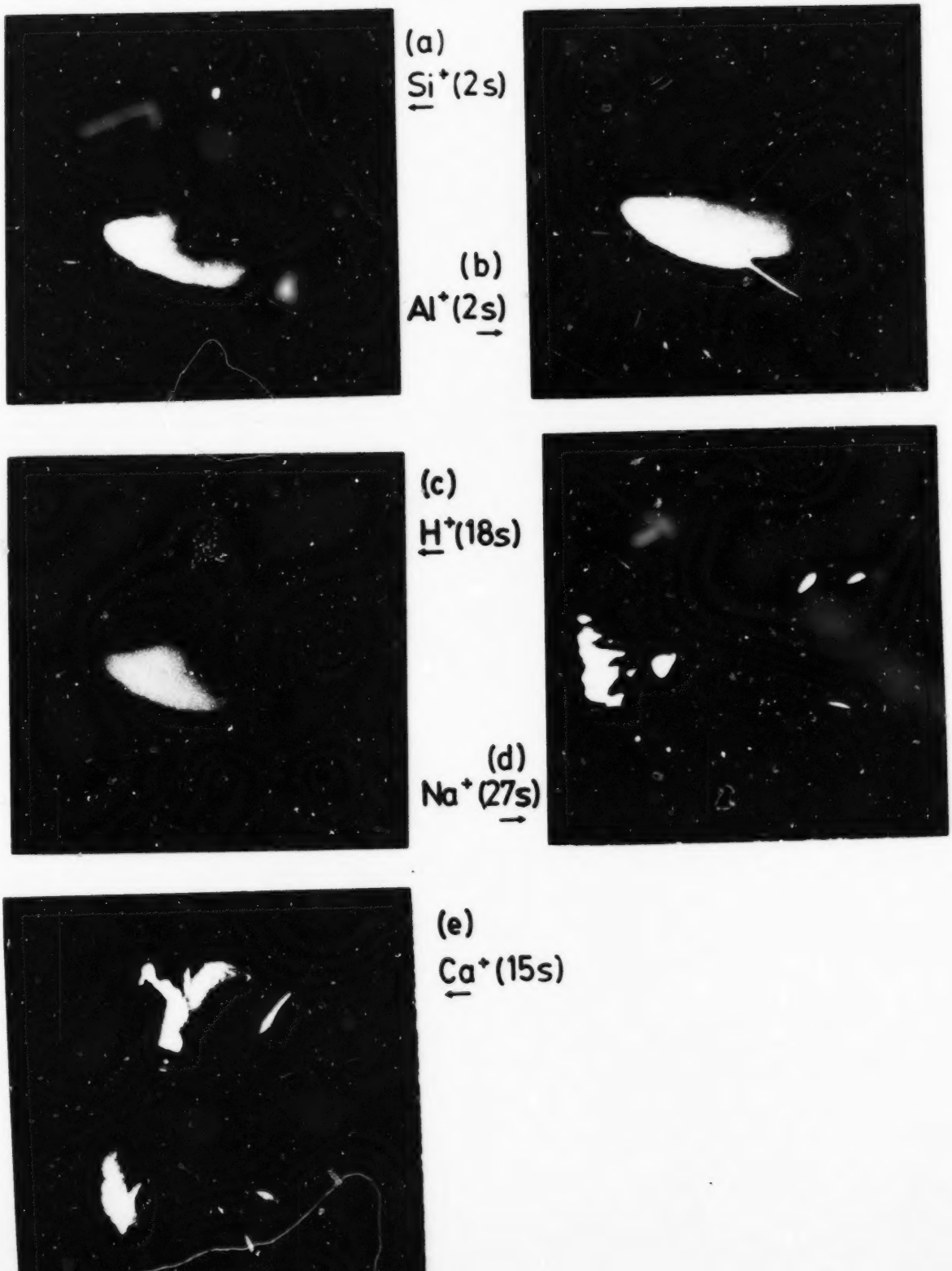

Figure 8

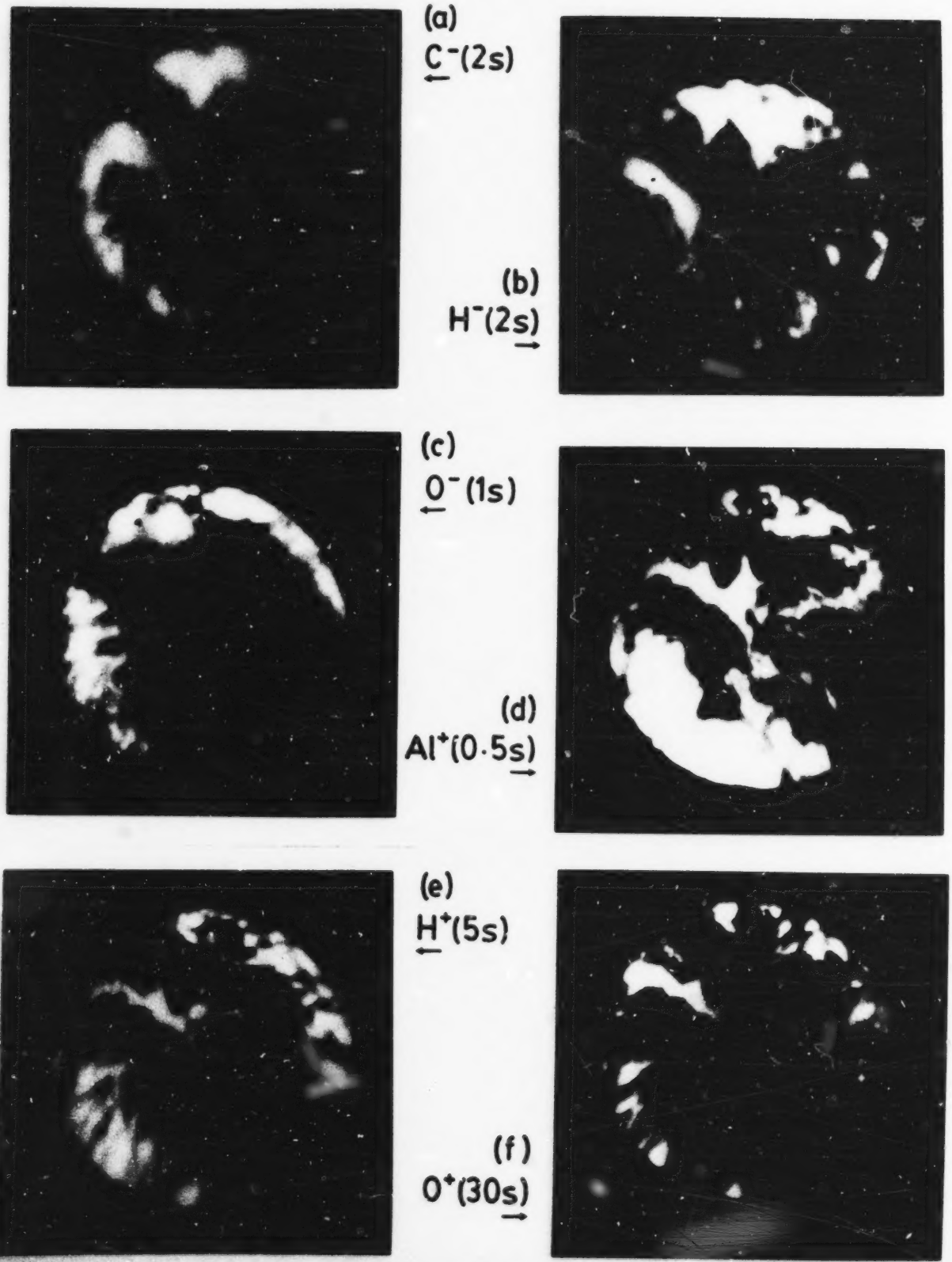

Figure 9

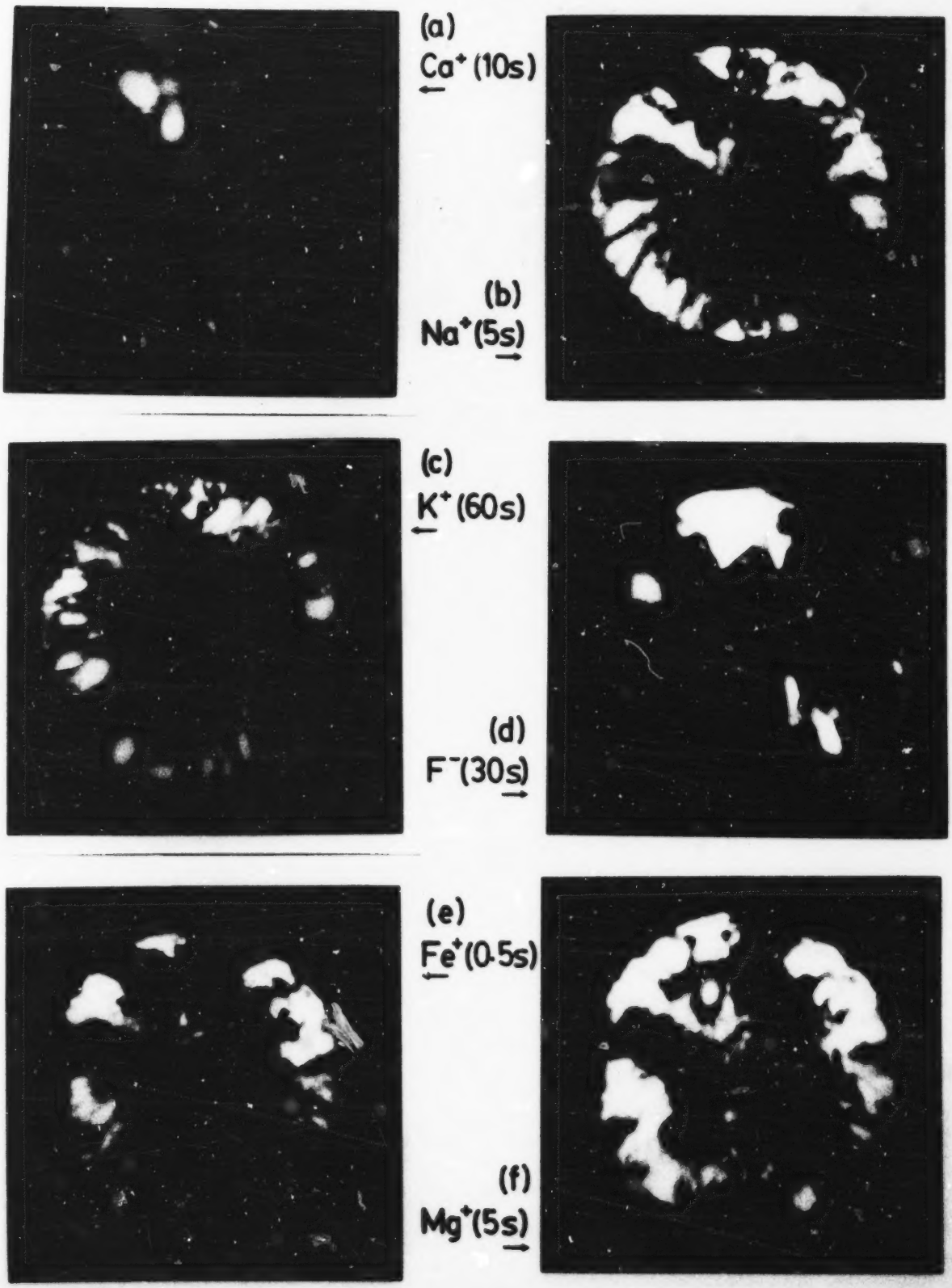

Figure 10